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Kinetic Theory of Vibrational Relaxation in a Radiation Field: The Optic–Acoustic Effect

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A microscopic derivation is presented of the rate equations governing vibrational relaxation occurring in the optic–acoustic effect. Detailed expressions applicable to the spectrophone experiment are given both for an excitation source consisting of a broadband radiation field and for laser-driven systems. It is clear from the present treatment that no real advantage accrues from the use of laser excitation sources in the standard spectrophone experiment, due to the resultant strong dependence of the driving force itself on the mechanical chopper frequency. For broadband radiation field the dependence on the chopper frequency is removed and the standard result containing the Einstein coefficient of induced absorption is recovered. The spectrophone response for the simplest case of a two-level system is given explicitly and its similarity to phenomenologically derived expressions is pointed out.

KEY WORDS: Kinetic theory; radiation-driven systems; rate equations; vibrational relaxation; optic–acoustic effect.

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1. INTRODUCTION

Most theories dealing with vibrational relaxation in molecular gases are based on the assumption that the translational and rotational degrees of freedom remain in equilibrium. Such an assumption is satisfactory when the transfer of translational and rotational energy to the surroundings of the system of interest (the heat bath in which the system is immersed) takes place easily. Moreover, experiments are frequently performed under conditions which are such that a small change in the translational and rotational temperature plays only a minor role: This serves to extend the validity of the traditional approaches. However, for the optic–acoustic effect the situation is quite different. In this case a radiation source excites the molecules into one of their accessible vibrational states and this is followed by a deexcitation due to collisions, the net result being that energy is fed into the translational and rotational degrees of freedom. Should the gas be enclosed in a constant volume, this, in turn, leads to a rise in pressure. When the incident beam of radiation is chopped and the pressure fluctuations are monitored by means of a microphone, an apparatus is obtained (the so-called spectrophone) which allows the determination of the corresponding vibrational relaxation times.

A theoretical description of such a phenomenon must contain the following two special features:

1. A coupling between the gaseous system and the radiation field which describes the excitation of vibrational states by the radiation field.
2. A coupling between the vibrational and translational–rotational degrees of freedom so that nonequilibrium pressure changes can be described.

In all presently existing theories the first of these conditions is met by introducing into a set of rate equations a production term containing the product BI of an Einstein B-coefficient and the radiation density I. The second feature is brought in by modeling the rate equations in a suitable way via the energy conservation law. Such an approach, although perhaps sufficient for a phenomenological description, is less satisfactory from a microscopic point of view. For instance, the interaction between the radiation field $\mathbf{E}$ and a molecule is described microscopically by the Hamiltonian $-\boldsymbol{\mu}\cdot\mathbf{E}$, $\boldsymbol{\mu}$ being the dipole-moment operator of the molecule. This, compared with the presence of the term BI (which is proportional to E^2) in the rate equations, would suggest that a microscopic theory should be carried through to second order in $\mathbf{E}$. Further, the Einstein B-coefficient only occurs in connection with a sufficiently broadband radiation field (see, for instance, Ref. 1) thus excluding the description of laser-driven systems. The present work, which is based on a suitable transport equation,(2) gives a microscopic derivation of the rate equations relevant for the description of the optic–acoustic effect. The resulting equations are applicable to both narrowband and broadband radiation fields. In the latter case the usual results containing the Einstein B-coefficient are recovered. Spontaneous radiation processes are not considered since these effects are essentially beyond the range of the semiclassical approach adopted here.

2. BASIC EQUATIONS

If the radiation field is sufficiently weak that saturation effects play no role, it is possible to expand the singlet density operator ρ about its equilibrium value $\rho^{(0)}$. Such will be assumed to be the case in this paper. In fact, rather than use ρ and $\rho^{(0)}$, it will be convenient to use the corresponding Wigner functions f and $f^{(0)}$: These quantities are Wigner functions as far as the translational degrees of freedom are concerned but remain operators in internal state space.

Thus, the assumption of a weak radiation field allows f to be written as

$$f = f^{(0)} + f^{(1)}(t), \qquad f^{(1)} \ll f^{(0)} \tag{1}$$

With this, the collision term in the transport equation(3) can be linearized and, in the impact approximation, the transport equation can be expressed as

$$\begin{aligned} \partial_t f^{(1)}(t) + iL^{(\mathrm{ext})}(t) f^{(1)}(t) &= \mathscr{J}^{(0)}(f^{(1)}(t) - f^{(0)}\beta\tilde{\boldsymbol{\mu}} \cdot \mathbf{E}(t)) \\ &\quad - iL^{(1)}(f^{(1)}(t) - f^{(0)}\beta\tilde{\boldsymbol{\mu}} \cdot \mathbf{E}(t)) \\ &\equiv \mathscr{J}(f^{(1)}(t) - f^{(0)}\beta\tilde{\boldsymbol{\mu}} \cdot \mathbf{E}(t)) \end{aligned} \tag{2}$$

with

$$L^{(\mathrm{ext})}(t)A = [-\boldsymbol{\mu} \cdot \mathbf{E}(t), A]_-, \qquad L^{(1)}A = [H, A]_- \tag{3}$$

The symbol β has the usual significance, $\beta = (kT)^{-1}$, and H is the internal state Hamiltonian for a single molecule. The Kubo transform $\tilde{A}$ of an operator A is defined as

$$\tilde{A} = \beta^{-1} \int_0^\beta e^{\lambda H} A e^{-\lambda H} \, d\lambda \tag{4}$$

while $\mathscr{J}^{(0)}$ is the linearized collision operator, identical to that used in Ref. 3, except that here the emphasis is on the vibrational degrees of freedom rather than on the rotational ones. Actually, Eq. (2) is equivalent to Eq. (3.13) of Ref. 3 with $f^{(1)}(t) = f^{(0)}(1 + \beta\tilde{\boldsymbol{\mu}} \cdot \mathbf{E}(t) + \tilde{\phi}(t))$, with the understanding that in the present case $f^{(1)}(t)$ is allowed to have nonvanishing matrix elements between states with different internal energies. The present form of $\mathscr{J}^{(0)}$ is a reasonable approximation for the case where the internal energy levels are sufficiently split[4,5] and the frequency ω of the radiation field remains close to one of the vibrational transition frequencies ω_0 of a molecule: i.e., $|(\omega - \omega_0)\,\tau_{\text{int}}| \ll 1$, where the interaction time τ_{int} stands for the average time that two particles interact during a binary collision. Outside this frequency region $\mathscr{J}^{(0)}$ is still dominant but frequency-dependent corrections to this collision operator start to build up. This could be important should a precise investigation of the wings of a spectral line be desired but it is not very significant for the present problem, where the field merely acts as a means of populating vibrational levels.

It should be noted that Eq. (2) as it stands refers to a spatially homogeneous system: Generalization to inhomogeneous systems is straightforward but will not be considered here. The Wigner functions f and $f^{(0)}$ are normalized according to

$$\operatorname{tr} f = \operatorname{tr} f^{(0)} = n, \qquad \operatorname{tr} f^{(1)} = 0 \tag{5}$$

where n is the number density. The symbol tr indicates a trace over the internal states and an integration over linear momentum. Let A_ω be an (internal state) operator with the property that it has nonvanishing matrix elements between states α and β with energy difference $\omega_\alpha - \omega_\beta = \omega$ (in units of $\hbar$) only. Then $\mathscr{J}^{(0)}$ has the property that A_ω is mapped into a quantity $B = \mathscr{J}^{(0)} A_\omega$ of the same type, i.e., $B = B_\omega$. Formally,

$$\mathscr{J}^{(0)} A_\omega = (\mathscr{J}^{(0)} A_\omega)_\omega\,; \qquad \mathscr{J}^{(0)}_{\omega\omega'} = \mathscr{J}^{(0)}_{\omega\omega}\,\delta(\omega, \omega') \tag{6}$$

[$\delta(a, b)$ is the Kronecker delta]. It will be assumed in the sequel that matrix elements of $\boldsymbol{\mu}$ between states with the same energy vanish. This is obviously not the case for molecules possessing a permanent dipole moment which is not perpendicular to the molecular rotational angular momentum (e.g., symmetric-top molecules). However, for such molecules the corresponding effect, a possible redistribution of the occupation probability over the degenerate substates of an internal energy level under the influence of the field $\mathbf{E}(t)$, does not play any role in the frequency region of interest in this work. Note also that this refers only to nonequilibrium effects since, due to the smallness of $\beta\boldsymbol{\mu}\cdot\mathbf{E}$, changes in the equilibrium distribution are negligible.

The property (6) of $\mathscr{J}^{(0)}$ together with the assumption just made about the dipole moment operator leads to a number of simplifications in the formalism. For this purpose a projector P which projects upon the part $(A_\omega)_{\omega=0}$ of an operator A, and its complement Q, are defined through

$$PA = \sum_\alpha \sum_\beta |\alpha\rangle\langle\alpha| A |\beta\rangle\langle\beta|\,\delta(\omega_\alpha, \omega_\beta), \qquad Q = 1 - P \tag{7}$$

where $| \alpha\rangle$ is an eigenstate of H. It is a simple matter to establish the following properties of these projectors:

$$P\mathscr{J} = \mathscr{J}P = P\mathscr{J}^{(0)} = \mathscr{J}^{(0)}P; \quad P\boldsymbol{\mu} = \mathbf{0}, \quad Q\boldsymbol{\mu} = \boldsymbol{\mu}; \quad PL^{(\mathrm{ext})}(t)P = 0 \tag{8}$$

These relations lead immediately to the decomposition of Eq. (2) into a pair of equations which are coupled only via the field term $L^{(\mathrm{ext})}(t)$:

$$\partial_t Pf^{(1)}(t) + iPL^{(\mathrm{ext})}(t)\, Qf^{(1)}(t) = \mathscr{J}^{(0)}Pf^{(1)}(t) \tag{9}$$

$$\partial_t Qf^{(1)}(t) + iQL^{(\mathrm{ext})}(t)f^{(1)}(t) = \mathscr{J}(Qf^{(1)}(t) - f^{(0)}\beta\tilde{\boldsymbol{\mu}}\cdot\mathbf{E}(t)) \tag{10}$$

To first order in the electric field, $Qf^{(1)}(t)$ can be obtained from Eq. (10) by omitting the second term on the left-hand side. This gives

$$\begin{aligned} Qf^{(1)}(t) = {} & \{\exp[\mathscr{J}(t - t_0)]\}\, Qf^{(1)}(t_0) \\ & - \int_{t_0}^{t} ds\{\exp[\mathscr{J}(t - s)]\}\, \mathscr{J}f^{(0)}\beta\tilde{\boldsymbol{\mu}}\cdot\mathbf{E}(s) \end{aligned} \tag{11}$$

which can be used to calculate (in the impact approximation) collision-broadened line profiles since these quantities are related to $\mathrm{tr}[Qf^{(1)}(t)]\boldsymbol{\mu}$. To the same order of approximation, $Pf^{(1)}(t)$ vanishes provided that the system was in equilibrium when $\mathbf{E}(t)$ was switched on. Since the occupation probabilities of the various internal states are given in terms of averages over $Pf^{(1)}(t)$, it follows that these quantities are unaffected by the field to first order in $\mathbf{E}(t)$. This result is not surprising since it is in essence due to the assumption $P\boldsymbol{\mu} = 0$: Indeed, the situation is entirely analogous to the vanishing of the first-order Stark effect for molecules possessing a dipole moment operator having only off-diagonal (in internal energy) matrix elements.

The second approximation to $Pf^{(1)}(t)$ is obtained by the substitution of Eq. (11) into Eq. (9). Now a nonvanishing result is obtained, in agreement with the phenomenological approach mentioned in the introduction where the radiation density, which is proportional to E^2, enters the theory. It is clear from the foregoing that at higher field intensities further approximations should be taken into account. Hence, in second approximation considering a system originally in equilibrium and with $\mathbf{E}(t)$ switched on adiabatically from $t_0 = -\infty$,

$$f^{(1)}(-\infty) = 0, \qquad \mathbf{E}(-\infty) = 0 \tag{12}$$

the resulting equation for $Pf^{(1)}(t)$ becomes

$$\partial_t Pf^{(1)}(t) - iPL^{(\mathrm{ext})}(t)\int_{-\infty}^{t} ds\{\exp[\mathscr{J}(t - s)]\}\, \mathscr{J}f^{(0)}\beta\tilde{\boldsymbol{\mu}}\cdot\mathbf{E}(s) = \mathscr{J}^{(0)}Pf^{(1)}(t) \tag{13}$$

with the (formal) solution

$$Pf^{(1)}(t) = \int_{-\infty}^{t} ds\{\exp[\mathscr{J}^{(0)}(t-s)]\}\, iPL^{(\text{ext})}(s)$$
$$\times \int_{-\infty}^{s} du\{\exp[\mathscr{J}(s-u)]\}\, \mathscr{J}f^{(0)}\beta\tilde{\mu}\cdot \mathbf{E}(u) \tag{14}$$

3. MODULATED SINUSOIDAL FIELDS

In this section Eqs. (13) and (14) are considered for the case where $\mathbf{E}(t)$ consists of a linearly polarized monochromatic radiation field modulated by a function $h(t)$,

$$E(t) = \mathbf{E}(\cos \omega t)\, h(t) \tag{15}$$

Should $h(t)$ also be sinusoidal, the overall situation would be simple. Actual spectrophones, however, make use of a mechanical chopping device and $h(t)$, although still periodic in time, may contain many Fourier components. Due to the nonlinear nature of the problem, high-frequency components in the Fourier spectrum of $h(t)$ may combine to contribute to a low-frequency component of $Pf^{(1)}(t)$. Denoting the period of $h(t)$ by Ω, this function can be represented as

$$h(t) = \sum_{n=-\infty}^{+\infty} h_n(\Omega/2\pi)^{1/2}\, e^{in\Omega t}; \qquad h_{-n} = \bar{h}_n \tag{16}$$

It will be assumed in the following that ω is much larger than Ω,

$$\omega \gg \Omega \tag{17}$$

This condition is always satisfied in actual experimental situations since there, ω is of the order of a typical vibrational transition frequency whereas Ω is varied through the range of the inverses of the vibrational relaxation times of interest. Now $\mathbf{E}(t)$ and $L^{(\text{ext})}(t)$ can be written as

$$\mathbf{E}(t) = \tfrac{1}{2}\mathbf{E} \sum_{n=-\infty}^{+\infty} (\Omega/2\pi)^{1/2}\, h_n\{\exp[i(\omega + n\Omega)t] + \exp[-i(\omega - n\Omega)t]\} \tag{18}$$

and

$$L^{(\text{ext})}(t) = \tfrac{1}{2}L^{(\text{ext})} \sum_{n=-\infty}^{+\infty} (\Omega/2\pi)^{1/2}\, h_n\{\exp[i(\omega + n\Omega)t] + \exp[-i(\omega - n\Omega)t]\} \tag{19}$$

The introduction of these expansions into Eq. (14) gives $Pf^{(1)}(t)$ as

$$\begin{aligned} Pf^{(1)}(t) = (\Omega/8\pi) \sum_m \sum_n h_m h_n \{ & K(\omega + m\Omega, \omega + n\Omega) + K(\omega + m\Omega, -\omega + n\Omega) \\ & + K(-\omega + m\Omega, \omega + n\Omega) + K(-\omega + m\Omega, -\omega + n\Omega)\} \end{aligned} \tag{20}$$

with $K(\omega_1, \omega_2)$ defined by

$$\begin{aligned} K(\omega_1, \omega_2) &\equiv \int_{-\infty}^{t} ds \{\exp[\mathscr{J}^{(0)}(t - s)]\}\, iPL^{(\mathrm{ext})} \exp(i\omega_1 s) \\ &\quad \times \int_{-\infty}^{s} du \{\exp[\mathscr{J}(s - u)]\}\, \mathscr{J} f^{(0)} \beta \tilde{\boldsymbol{\mu}} \cdot \mathbf{E} \exp(i\omega_2 u) \\ &= i\{\exp[i(\omega_1 + \omega_2)t]\}[-\mathscr{J}^{(0)} + i(\omega_1 + \omega_2)]^{-1}\, PL^{(\mathrm{ext})} \\ &\quad \times (-\mathscr{J} + i\omega_2)^{-1}\, \mathscr{J} f^{(0)} \beta \tilde{\boldsymbol{\mu}} \cdot \mathbf{E} \end{aligned} \tag{21}$$

In obtaining the final form for $K(\omega_1, \omega_2)$, it has been assumed that there are no contributions from the lower limits in the two integrations. This presupposes some form of weak ergodicity for $[\exp(\mathscr{J}t)]\, \tilde{\boldsymbol{\mu}}$, i.e.,

$$\lim_{t \to \infty} \operatorname{tr} f^{(0)}\{[\exp(\mathscr{J}t)]\tilde{\boldsymbol{\mu}}\}A = 0$$

for certain A (and similarly for $\mathscr{J}^{(0)}$ instead of $\mathscr{J}$). This will in fact be the case whenever the assumption $P\boldsymbol{\mu} = 0$ is a valid one, since the only eigenfunctions of $\mathscr{J}^{(0)}$ and $\mathscr{J}$ at the eigenvalue zero are the summational invariants (particle number, linear momentum, and the free-particle energy).

Inspection of Eq. (21) shows that, due to the presence of the resolvent $[-\mathscr{J}^{(0)} + i(\omega_1 + \omega_2)]^{-1}$, the first and last terms between the curly brackets in Eq. (20) may be neglected. For these two terms the resolvent is approximately equal to $(-\mathscr{J}^{(0)} \pm 2i\omega)^{-1}$ and, since ω is very large, it becomes negligible (rotating wave approximation). Hence $Pf^{(1)}(t)$ can be reduced to

$$\begin{aligned} Pf^{(1)}(t) &= \sum_{m=-\infty}^{+\infty} \sum_{n=-\infty}^{+\infty} (\Omega/2\pi)\, h_m h_n \{\exp[i(m + n)\,\Omega t]\}[-\mathscr{J}^{(0)} + i(m + n)\Omega]^{-1} \\ &\qquad \times \tfrac{1}{4} iPL^{(\mathrm{ext})}\{[-\mathscr{J} + i(-\omega + n\Omega)]^{-1} \\ &\qquad + [-\mathscr{J} + i(\omega + n\Omega)]^{-1}\}\, \mathscr{J} f^{(0)} \beta \tilde{\boldsymbol{\mu}} \cdot \mathbf{E} \\ &= (\Omega/2\pi) \sum_{m=-\infty}^{+\infty} [\exp(im\Omega t)](-\mathscr{J}^{(0)} + im\Omega)^{-1}(i/4)\, PL^{(\mathrm{ext})} \sum_{n=-\infty}^{+\infty} h_{m-n} h_n \\ &\qquad \times \{[-\mathscr{J} + i(-\omega + n\Omega)]^{-1} + [-\mathscr{J} + i(\omega + n\Omega)]^{-1}\}\, \mathscr{J} f^{(0)} \beta \tilde{\boldsymbol{\mu}} \cdot \mathbf{E} \\ &\equiv (\Omega/2\pi) \sum_{m=-\infty}^{+\infty} [\exp(im\Omega t)] f_m \end{aligned} \tag{22}$$

in which the final line serves as a definition of f_m. It follows that $f_m = f_m(\Omega, \omega)$ obeys the equation

$$A_m = (\mathscr{J}^{(0)} - im\Omega) f_m \tag{23}$$

where

$$A_m(\Omega, \omega) = -(i/4)\, PL^{(\mathrm{ext})} \sum_{n=-\infty}^{+\infty} h_{m-n} h_n \{[-\mathscr{J} + i(-\omega + n\Omega)]^{-1} + [-\mathscr{J} + i(\omega + n\Omega)]^{-1}\} \mathscr{J} f^{(0)} \beta \boldsymbol{\mu} \cdot \mathbf{E} \tag{24}$$

Equations (23) possess a solution since A_m is orthogonal to the summational invariants. This result follows directly from the presence in A_m of $L^{(\mathrm{ext})}$. In fact, Eq. (23) has, apart from the term $-im\Omega$, the structure of the well-known Chapman–Enskog equations of kinetic theory [a similar situation was encountered in Ref. 3, Eq. (3.23)]. The time-dependent version of Eq. (23) for $f_m(t) = f_m e^{im\Omega t}$ is

$$\partial_t f_m(t) = \mathscr{J}^{(0)} f_m(t) - e^{im\Omega t} A_m(\Omega, \omega) \tag{25}$$

In this equation, the final term on the right-hand side acts as a driving force. It is worth noting that, due to the dependence of A_m on Ω, the final result for the nonequilibrium pressure may become more complicated than in phenomenological theories. To get an idea of what actually happens, consider the diagonal elements of the resolvents in Eq. (24). These quantities have the structure

$$[\tau^{-1} + i(\omega_{\alpha\beta} - \omega + n\Omega)]^{-1} \tag{26}$$

Here $\mathscr{J}^{(0)}$ has been replaced by the relaxation frequency (inverse relaxation time) τ^{-1}, while the transition frequency $\omega_{\alpha\beta} = \omega_\alpha - \omega_\beta$ has derived from the term $-iL^{(1)}$. Since τ^{-1}, being a measure for the width of the pressure-broadened vibrational line centered at $\omega_{\alpha\beta}$, is proportional to the number density, it can be seen that for low densities a sharp peak occurs for ω close to $\omega_{\alpha\beta} + n\Omega$: For this particular value of ω but for other values of $n\Omega$, the mismatch between the frequencies will soon be large enough to make the expression (26) quite small. From this, it must be expected that $A_m(\Omega)$ will depend strongly on Ω, thus making a monochromatic radiation field less useful for the determination of vibrational relaxation times than might have been expected. Experimentally, these vibrational relaxation times are determined from phase-shift or amplitude measurements and, in the case of a monochromatic radiation field, the driving force itself already shows a phase shift and an amplitude depending on Ω.

The situation is different, however, for a radiation source having a broadband spectrum of incoherent radiation. For such a case the overall magnitude of $f^{(1)}(t)$ is obtained by the integration of Eq. (22) over the band. In the event that the field strength does not vary appreciably over the band, the Ω dependence of A_m is removed and the usual result, featuring the Einstein B-coefficient, is recovered. The actual calculation for this case is presented in Section 5.

4. RATE EQUATIONS

For the purpose of further discussion it is convenient to write $Pf^{(1)}(t)$ as

$$Pf^{(1)}(t) = f^{(0)}\phi(t) = f^{(0)} \sum_m \phi_m(t) = f^{(0)} \sum_m \phi_m(\Omega, \omega) e^{im\Omega t} \qquad (27)$$

Implicit in this form for $Pf^{(1)}(t)$ is the neglect of any possible vibration–rotation interactions since then the equilibrium Wigner function-density operator factorizes into separate translational, and vibrational parts,

$$f^{(0)} = n[\exp(-\beta H^{(0)})]/\mathrm{tr}\exp(-\beta H^{(0)}) = nf^{(\mathrm{t})}f^{(\mathrm{r})}f^{(\mathrm{v})} \qquad (28)$$

and it follows from the form of (28) that necessarily $\phi_m = P\phi_m$ for each m.

Now a suitable series expansion for ϕ_m will be made and the corresponding expansion coefficients will be interpreted as certain macroscopic quantities. As usual in kinetic theory, a truncation of this expansion will be made in order to obtain a closed set of coupled moment equations known as the relaxation or rate equations. For the optic–acoustic effect the relevant macroscopic variables are the pressure (and hence the kinetic energy) and the populations of the various vibrational states. It has been assumed here that translation and rotation remain in mutual equilibrium so that the sum $H^{(\mathrm{t+r})}$ of the translational and rotational energies must be included in the series expansion instead of the translational energy $H^{(\mathrm{t})}$ alone.

In what follows the inner product and norm defined by

$$(A, B) \equiv n^{-1}\,\mathrm{tr} f^{(0)}AB^{\dagger}, \qquad \| A \| \equiv (A, A)^{1/2} \qquad (29)$$

and the equilibrium average defined by

$$\langle A \rangle_0 \equiv n^{-1}\,\mathrm{tr} f^{(0)}A = (A, 1) \qquad (30)$$

will be extensively used. The (truncated) series expansion proposed is

$$\varphi_0 = \beta(H^{(\mathrm{t+r})} - \langle H^{(\mathrm{t+r})}\rangle_0), \qquad \varphi_k = \sum_\alpha | \alpha\rangle\langle\alpha | \,\delta(\omega_\alpha, \omega_k), \qquad k > 0 \quad (31)$$

from which φ_k, $k > 0$, is seen to be the projection onto the subspace spanned by the vibrational eigenstates with energy $\hbar\omega_k$, with $\hbar\omega_k$ running through all vibrational energy eigenvalues for $k = 1, 2, 3, \ldots$. A direct calculation shows that the φ_k are mutually orthogonal with respect to the inner product (29), their norms being given by

$$\begin{aligned} \| \varphi_0 \|^2 &= C_v^{(\mathrm{t+r})}/k = \beta^2 \langle (H^{(\mathrm{t+r})})^2 - \langle H^{(\mathrm{t+r})} \rangle_0^2 \rangle_0 \\ \| \varphi_k \|^2 &= x_k^{(0)} = g_k [\exp(-\beta \hbar \omega_k)] \Big/ \sum_\alpha \exp(-\beta \hbar \omega_\alpha) \end{aligned} \tag{32}$$

The quantity $C_v^{(\mathrm{t+r})}$ is the sum of the translational and rotational specific heats per particle at constant volume, while $x_k^{(0)}$ is the equilibrium fraction of particles with vibrational energy $\hbar\omega_k$, g_k denoting the multiplicity of the level designated by k.

The expansion for ϕ_m now reads

$$\phi_m(\omega, \Omega) = \sum_k a_{mk} \varphi_k : \qquad a_{-m,k} = \bar{a}_{mk} \tag{33}$$

It is a simple task, now, to obtain a physical interpretation of the various expansion coefficients a_{mk}. First, defining the nonequilibrium temperature $T + \Delta T$ (where T is the equilibrium temperature occurring in $f^{(0)}$) by means of the expectation value of the translational energy,

$$\tfrac{3}{2} nk(T + \Delta T) = \operatorname{tr} f H^{(\mathrm{t})} \tag{34}$$

it is found that

$$\begin{aligned} \tfrac{3}{2} nk(T + \Delta T) &= \operatorname{tr} f^{(0)}(1 + \phi(t))\, H^{(\mathrm{t})} \\ &= \tfrac{3}{2} nkT + n \sum_m \sum_k a_{mk} e^{im\Omega t} (\varphi_k , H^{(\mathrm{t})}) \\ &= \tfrac{3}{2} nkT \Big(1 + \sum_m a_{m0} e^{im\Omega t}\Big) \end{aligned}$$

Writing the fractional deviation $\Delta\hat{T}$ as

$$\Delta\hat{T} \equiv \Delta T/T = \sum_m \Delta\hat{T}_m(t) = \sum_m \Delta\hat{T}_m e^{im\Omega t} \tag{35}$$

it follows that

$$a_{m0} = \Delta\hat{T}_m \tag{36}$$

and hence the contribution of the component at frequency $| m\Omega |$ to the overall relative deviation of the temperature from its equilibrium value is given by

$$\Delta\hat{T}_{|m|}(t) = a_{m0}\, e^{im\Omega t} + a_{-m0}\, e^{-im\Omega t} \tag{37}$$

The population density $n_k = nx_k$ of the fraction of particles with vibrational energy $\hbar\omega_k$ is given by the expectation value of φ_k $(k > 0)$:

$$\begin{aligned} n_k = nx_k &= \operatorname{tr} f\varphi_k = \operatorname{tr} f^{(0)}[1 + \phi(t)]\,\varphi_k \\ &= nx_k^{(0)}\left(1 + \sum_m a_{mk}e^{im\Omega t}\right) \end{aligned}$$

Hence, defining the fractional deviation $\Delta\hat{x}_k$ by

$$\Delta\hat{x}_k \equiv (x_k - x_k^{(0)})/x_k^{(0)} = \sum_m \Delta\hat{x}_{mk}(t) = \sum_m \Delta\hat{x}_{mk}\, e^{im\Omega t} \tag{38}$$

it is found that the expansion coefficients a_{mk} are given as

$$a_{mk} = \Delta\hat{x}_{mk} \tag{39}$$

and, analogously to Eq. (37), $\Delta\hat{x}_{|m|k}(t)$ is given by

$$\Delta\hat{x}_{|m|k}(t) = a_{mk}\, e^{im\Omega t} + a_{-mk}\, e^{-im\Omega t} \tag{40}$$

With the above results the expansion for $f_m = f^{(0)}\phi_m$ can be rewritten as

$$f_m = f^{(0)}\left(\Delta\hat{T}_m\varphi_0 + \sum_{k>0} \Delta\hat{x}_{mk}\varphi_k\right) \tag{41}$$

Notice, however, that because of Eq. (5), the $\Delta\hat{x}_{mk}$ are subject to the subsidiary condition

$$\sum_{k>0} x_k^{(0)}\, \Delta\hat{x}_{mk} = 0 \tag{42}$$

Introduction of the function (41) into Eq. (23) and the consequent formation of moments with respect to each of the φ_k's yields the set of equations

$$\begin{aligned} [\mathscr{I}_{00} - im\Omega(C_v^{(\mathrm{t+r})}/k)]\,\Delta\hat{T}_m + \sum_{l>0} \mathscr{I}_{0l}\,\Delta\hat{x}_{ml} &= 0 \\ \mathscr{I}_{k0}\,\Delta\hat{T}_m + \sum_{l>0} \mathscr{I}_{kl}\,\Delta\hat{x}_{ml} - im\Omega x_k^{(0)}\,\Delta\hat{x}_{mk} &= W_{mk} \end{aligned} \tag{43}$$

where

$$\mathscr{I}_{kl} = (\varphi_k\,, \mathscr{I}^{(0)}\varphi_l), \qquad W_{mk} = n^{-1}\operatorname{tr} A_m\varphi_k \tag{44}$$

Here use has been made of the fact that $f^{(0)}$ can be pulled through $\mathscr{I}^{(0)}$. Note that W_{m0} vanishes since φ_0 does not depend upon the vibrational degrees of freedom, so that $L^{(\mathrm{ext})}\varphi_0 = 0$. This may be expressed in another way by saying that the radiation field does not directly affect the translational (or rotational) degrees of freedom.

The time-dependent equations corresponding to Eqs. (43) are

$$
\begin{aligned}
(C_v^{(t+r)}/k)\,\partial_t \Delta\hat{T}_m(t) &= \mathscr{J}_{00}\,\Delta\hat{T}_m(t) + \sum_{l>0} \mathscr{J}_{0l}\,\Delta x_{ml}(t) \\
x_k^{(0)}\,\partial_t \Delta\hat{x}_{mk}(t) &= \mathscr{J}_{00}\,\Delta\hat{T}_m(t) + \sum_{l>0} \mathscr{J}_{kl}\,\Delta\hat{x}_{ml}(t) - W_{mk}e^{im\Omega t}
\end{aligned}
\tag{45}
$$

The relaxation coefficients $\mathscr{J}_{kl}$ which were introduced in Eq. (44) are not all independent and satisfy a number of auxiliary conditions. First, since $\sum_{k>0} \varphi_k = I$, the identity operator, which is a summational invariant, it follows that

$$\sum_{k>0} \mathscr{J}_{kl} = \sum_{l>0} \mathscr{J}_{kl} = 0 \tag{46}$$

This is simply a consequence of the conservation of particle number. Second, in a similar manner, the conservation of the total free-particle energy (translational, rotational, and vibrational) results in the summational invariance of $H^{(0)} = H^{(t)} + H^{(r)} + H^{(v)}$ and hence of ψ given as

$$\psi = \varphi_0 + \sum_{k>0} \beta\hbar\omega_k\varphi_k \tag{41}$$

This, in turn, leads to the relations

$$\mathscr{J}_{00} = (\beta\hbar)^2 \sum_{k>0}\sum_{l>0} \omega_k\omega_l\mathscr{J}_{kl}\,, \qquad \mathscr{J}_{k0} = \mathscr{J}_{0k} = -\beta\hbar \sum_{l>0} \omega_l\mathscr{J}_{lk}\,, \qquad k > 0 \tag{48}$$

From these results it follows that

$$a^{(1)} = (0, 1, 1, 1,\ldots), \qquad a^{(2)} = (1, \beta\hbar\omega_1, \beta\hbar\omega_2,\ldots) \tag{49}$$

are eigenvectors of the matrix $\mathscr{J}_{kl}$ with eigenvalue zero. This means that, within the present approximation, a system consisting of particles with N different vibrational levels possesses at most $N - 1$ different relaxation times (nonvanishing eigenvalues of $\mathscr{J}_{kl}$; $k, l > 0$).

For the description of the optic–acoustic effect, the temporal behavior of the nonequilibrium pressure

$$\Delta p(t) = p(t) - p = p(t) - nkT = p\,\Delta\hat{T}(t) \tag{50}$$

is important. It is seen from the results obtained so far that $\Delta p(t)$ is the sum of Fourier components at the frequencies $m\Omega$. From the first of Eqs. (43) it follows that $\Delta\hat{T}_m$ is related to the $\Delta\hat{x}_{ml}$ by

$$\Delta\hat{T}_m = [im\Omega(C_v^{(t+r)}/k) - \mathscr{J}_{00}]^{-1} \sum_{l>0} \mathscr{J}_{0l}\,\Delta\hat{x}_{ml} \tag{51}$$

while elimination of $\mathit{\Delta}\hat{T}_m$ from the remaining equations results in

$$im\omega x_k^{(0)}\,\mathit{\Delta}\hat{x}_{mk} = \sum_l K_{kl}(m\Omega)\,\mathit{\Delta}\hat{x}_{ml} + W_{mk} \tag{52}$$

where

$$K_{kl}(m\Omega) = \mathscr{J}_{kl} + \mathscr{J}_{k0}[im\Omega(C_v^{(\mathrm{t+r})}/k) - \mathscr{J}_{00}]^{-1}\,\mathscr{J}_{0l} \tag{53}$$

These equations give a complete description of the optic–acoustic effect. In practice, some further simplifications usually occur. For example, the magnitudes of some of the $\mathscr{J}_{kl}$ can be quite different from those of the remaining ones: This would allow a perturbation treatment of the equations. Moreover, under the usual experimental conditions it is often the case that only one W_{mk} is nonvanishing.

The present form of the rate equations (52) deviates from that customarily given due to the presence in Eq. (53) of the second term on the right-hand side. At high frequencies Ω this term as well as $\mathit{\Delta}\hat{T}_m$ vanishes: This is consistent with the fact that the translational and rotational degrees of freedom are no longer able to follow the rapid fluctuations in the populations of the vibrational levels.

5. BROADBAND RADIATION FIELDS

This section deals with the case when the driving force W_{mk} introduced in Eq. (44) arises from a broadband radiation field. In order to maintain a simple notation, the specific case of linear molecules will be considered: The rotational quantum numbers are here J and M. For more complicated molecules the extension is straightforward but of a greater notational complexity.

Within the present context only that part of a vibrational band is of interest for which the rotational levels have a significant equilibrium population. Thus, for a specific transition frequency

$$\omega_{kJlJ'} = \omega_{kJ} - \omega_{lJ'}\,, \qquad \mathit{\Delta}J = 0, \pm 1$$

J and J' must remain smaller than a given maximal value. The radiation field is now required to extend at least over this part of the band with a constant intensity. In particular, it covers each (collision-broadened) individual line in this part of the band. The quantities A_m, as defined by Eq. (24), will be written as

$$A_m = -\tfrac{1}{4}iL^{(\mathrm{ext})}\mathscr{F}(\mathscr{J})f^{(0)}\beta\tilde{\boldsymbol{\mu}}\cdot\mathbf{E} = -\tfrac{1}{4}iPL^{(\mathrm{ext})}f^{(0)}\beta[\mathscr{F}(\mathscr{J})\boldsymbol{\mu}]^{\sim}\cdot\mathbf{E} \tag{54}$$

where

$$\mathscr{F}(\mathscr{J}) = \sum_n h_{m-n}h_n\{[-\mathscr{J} + i(-\omega + n\Omega)]^{-1} + [-\mathscr{J} + i(\omega + n\Omega)]^{-1}\}\mathscr{J} \tag{55}$$

The final equality of Eq. (54) follows from the fact that $f^{(0)}$ can be pulled through $\mathscr{F}(\mathscr{J})$ and that the operation of taking the Kubo transform commutes with $\mathscr{J}$ and hence with $\mathscr{F}(\mathscr{J})$. Expression (44) for $W_{m,k}$ when written out is

$$\begin{aligned} W_{m,k} &= n^{-1} \operatorname{tr} A_m\varphi_k \\ &= -\tfrac{1}{4}in^{-1} \operatorname{tr}\{(L^{(\mathrm{ext})}f^{(0)}\beta[\mathscr{F}(\mathscr{J})\boldsymbol{\mu}]^{\sim} \cdot \mathbf{E})\, \varphi_k\} \\ &= \tfrac{1}{4}i(n\hbar)^{-1} \operatorname{tr}\{(\boldsymbol{\mu} \cdot \mathbf{E}f^{(0)}\beta[\mathscr{F}(\mathscr{J})\boldsymbol{\mu}]^{\sim} \cdot \mathbf{E} - f^{(0)}\beta[\mathscr{F}(\mathscr{J})\boldsymbol{\mu}]^{\sim} \cdot \mathbf{E}\boldsymbol{\mu} \cdot \mathbf{E})\varphi_k\} \end{aligned} \tag{56}$$

which can be simplified by insertion of the relation $\sum_l \varphi_l = I$ in the following way:

$$\begin{aligned} W_{m,k} = &-\frac{1}{4}\, i(n\hbar)^{-1} \operatorname{tr} \Big\{\boldsymbol{\mu} \cdot \mathbf{E} \sum_l \varphi_l f^{(0)}\beta[\mathscr{F}(\mathscr{J})\boldsymbol{\mu}]^{\sim} \cdot \mathbf{E}\varphi_k \\ &- f^{(0)}\beta[\mathscr{F}(\mathscr{J})\boldsymbol{\mu}]^{\sim} \cdot \mathbf{E} \sum_l \varphi_l\boldsymbol{\mu} \cdot \mathbf{E}\varphi_k\Big\} \\ = &-\frac{1}{12}\, iE^2(n\hbar)^{-1} \sum_l \operatorname{tr} f^{(0)}\beta(\mathscr{F}\boldsymbol{\mu})^{\sim} \cdot \{\varphi_k\boldsymbol{\mu}\varphi_l - \varphi_l\boldsymbol{\mu}\varphi_k\} \\ = &\sum_l W_{m,kl} \end{aligned} \tag{57}$$

Here use has been made of the isotropy of $\mathscr{J}$ and $\mathscr{F}(\mathscr{J})$ to reduce the tensorial dependence on $\mathbf{E}$ to a scalar one on E^2. Upon evaluation of the trace, the following result for $W_{m,kl}$ is obtained:

$$\begin{aligned} W_{m,kl} = &(i/12n\hbar^2)\, E^2 \int d\mathbf{p} \sum_{\alpha JM} \sum_{\alpha' J' M'} (f_{\alpha J}^{(0)} - f_{\alpha' J'}^{(0)})(\omega_{\alpha J} - \omega_{\alpha' J'})^{-1} \\ &\times (\mathscr{F}\boldsymbol{\mu})_{\alpha JM,\alpha' J' M'} \cdot \boldsymbol{\mu}_{\alpha' J' M',\alpha JM}\{\delta(\omega_{\alpha'}, \omega_k)\, \delta(\omega_\alpha, \omega_l) \\ &- \delta(\omega_{\alpha'}, \omega_l)\, \delta(\omega_\alpha, \omega_k)\} \\ = &(i/12n\hbar^2)\, E^2 \int d\mathbf{p} \sum_{\alpha JM} \sum_{\alpha' J' M'} \delta(\omega_\alpha, \omega_k)\, \delta(\omega_{\alpha'}, \omega_l)(f_{\alpha J}^{(0)} - f_{\alpha' J'}^{(0)}) \\ &\times (\omega_{\alpha J} - \omega_{\alpha' J'})^{-1}\{\boldsymbol{\mu}_{\alpha JM,\alpha' J' M'} \cdot (\mathscr{F}\boldsymbol{\mu})_{\alpha' J' M',\alpha JM} \\ &- (\mathscr{F}\boldsymbol{\mu})_{\alpha JM,\alpha' J' M'} \cdot \boldsymbol{\mu}_{\alpha' J' M',\alpha JM}\} \end{aligned} \tag{58}$$

where

$$f^{(0)}_{\alpha J} = n f^{(t)}(\mathbf{p}) f^{(r)}_{JM,JM} f^{(v)}_{\alpha\alpha} \tag{59}$$

If it is now assumed that the radiation field is of the broadband type in the sense mentioned previously and is centered about $\omega_{kl} = \omega_k - \omega_l$, the overall strength of $W_{m,kl}$ is obtained by integration over ω according to

$$\begin{aligned} E^2\mathscr{F}(\mathscr{J}) &\to \int \mathscr{F}(\mathscr{J}, \omega)\, 8\pi\rho(\nu)\, d\nu = \int \mathscr{F}(\mathscr{J}, \omega)\, 4I(\omega)\, d\omega \\ &\approx 4I(\omega_{kl}) \int_{\text{band}} \mathscr{F}(\mathscr{J}, \omega)\, d\omega \end{aligned} \tag{60}$$

In obtaining the final approximated result, the field intensity $I = I(\omega_{kl})$ has been assumed to be constant over the band. Since the integral over the band of $\mathscr{F}(\mathscr{J}, \omega)$ reduces to

$$\int_{\text{band}} d\omega[\tau^{-1} + i(\omega_{kl} - \omega + n\Omega)]^{-1} \approx \begin{cases} \pi, & \omega_{kl} > 0 \\ 0, & \omega_{kl} < 0 \end{cases} \tag{61}$$

it follows [e.g., by making the approximation (26)] that

$$E^2\mathscr{F}(\mathscr{J}) \to 4\pi I \sum_n h_{m-n} h_n (i/\hbar)[H, \ldots]_- \tag{62}$$

where the small dissipative part in $\mathscr{J}$ due to $\mathscr{J}^{(0)}$ has been neglected as compared with the commutator term (with magnitude ω_{kl}). Substitution of this result into Eq. (58) yields

$$\begin{aligned} W_{m,kl} &= (2\pi I/3\hbar^2) \sum_n h_{m-n} h_n \int d\mathbf{p} \sum_{\alpha JM} \sum_{\alpha' J' M'} \delta(\omega_\alpha, \omega_k)\, \delta(\omega_{\alpha'}, \omega_l) \\ &\quad \times (f^{(0)}_{\alpha J} - f^{(0)}_{\alpha' J'})\, \boldsymbol{\mu}_{\alpha JM, \alpha' J' M'} \cdot \boldsymbol{\mu}_{\alpha' J' M', \alpha JM} \\ &= (2\pi I/3\hbar^2) \sum_n h_{m-n} h_n (x^{(0)}_k - x^{(0)}_l) \mid \mu_{kl} \mid^2 \end{aligned} \tag{63}$$

The final form of this equation follows from the factorization

$$\boldsymbol{\mu}_{\alpha JM, \alpha' J' M'} = \mu^{(v)}_{\alpha\alpha'} \boldsymbol{\mu}^{(r)}_{JM, J'M'}$$

so that

$$
\begin{aligned}
&\int d\mathbf{p} \sum_{\alpha JM} \sum_{\alpha' J' M'} (f_{\alpha J}^{(0)} - f_{\alpha' J'}^{(0)})\, \delta(\omega_\alpha, \omega_k)\, \delta(\omega_{\alpha'}, \omega_l)\, \boldsymbol{\mu}_{\alpha JM,\alpha' J' M'} \cdot \boldsymbol{\mu}_{\alpha' J' M',\alpha JM} \\
&\quad = \sum_{\alpha JM} \sum_{\alpha' J' M'} (x_k^{(0)} f_J^{(0)} - x_l^{(0)} f_{J'}^{(0)})\, \delta(\omega_\alpha, \omega_k)\, \delta(\omega_{\alpha'}, \omega_l)\, | \mu_{\alpha\alpha'}^{(\mathrm{v})} |^2 \\
&\quad \times \boldsymbol{\mu}_{JM,J'M'}^{(\mathrm{r})} \cdot \boldsymbol{\mu}_{J'M',JM}^{(\mathrm{r})} \\
&\quad = (x_k^{(0)} - x_l^{(0)}) \sum_{\alpha\alpha'} \delta(\omega_\alpha, \omega_k)\, \delta(\omega_{\alpha'}, \omega_l)\, | \mu_{\alpha\alpha'}^{(\mathrm{v})} |^2 \\
&\quad \times \sum_{JM} \sum_{J'M'} f_J^{(0)} \boldsymbol{\mu}_{JM,J'M'}^{(\mathrm{r})} \cdot \boldsymbol{\mu}_{J'M',JM}^{(\mathrm{r})} \qquad (64)
\end{aligned}
$$

From this, $| \boldsymbol{\mu}_{kl} |^2$ is seen to be the square of the dipole moment matrix element for the transition $k \leftrightarrow l$, summed over the degenerate substates with nonvanishing dipole moment matrix elements (if any) and Boltzmann-averaged over the rotational fine structure.

6. DISCUSSION

A microscopic derivation of the rate equations governing the optic–acoustic effect has been given. The set of rate equations obtained for a many-vibrational-level system, Eqs. (43) or (45), has been expressed in terms of the temperature fluctuations $\Delta \hat{T}_m$ arising from the mth Fourier components of the modulating mechanical chopper employed in the spectrophone and the corresponding fluctuations $\Delta \hat{x}_{mk}$ of the fractional populations of the various vibrational levels (labeled by the subscript k). Since the treatment presented here has not employed the Einstein B-coefficient and is hence not restricted to broadband radiation fields, the equations are also appropriate to a description of laser-driven systems. One conclusion which may be drawn with respect to such systems is that no real advantage is obtained in the actual spectrophone experiments by employing a laser in order to excite the vibrational levels of interest. However, it is also clear from the present description that in the limit where no chopper is employed the absorption line for laser excitation can be studied. This absorption line will be of the simple Lorentzian type centered at the excitation frequency $\omega_{\alpha\beta}$.

As is shown in the appendix, the matrix elements of the collision operator between two vibrational states labeled by k and l [see Eq. (44)] can be written in terms of rate coefficients $k_{ij\to mn}$ associated with the transition of two molecules from the initial pair-state $| ij\rangle$ to the final pair-state $| mn\rangle$ as

$$\mathscr{I}_{kl} = (\mathscr{I}^{(0)}\varphi_l\,,\ \varphi_k) = n \sum_{r,s} \{x_k^{(0)} x_r^{(0)}(k_{kr\to ls} + k_{kr\to sl}) - x_r^{(0)} x_s^{(0)}(k_{rs\to kl} + \delta_{kl} k_{kr\to lm})\} \tag{65}$$

where n is the number density of the gas. The calculation presented in the appendix has assumed nondegenerate vibrational levels: In the case of vibrational degeneracy, weight factors will occur in the vibrational part of the equilibrium distribution function and it becomes a fairly simple matter of bookkeeping to arrive at a more general result. The result (65) corresponds to that obtained by Brau.(6) The rate coefficients can, in turn, be expressed in terms of degeneracy-averaged collision cross sections(7) as (see the appendix)

$$k_{ij\to mn} = (8\pi/m) \int_0^\infty dq\, q^3 f_{\mathrm{rel}}^{(0)}(q)\, \bar\sigma^{(\mathrm{tot})}(qij \to q'mn) \tag{66}$$

where q is the magnitude of the reduced relative momentum of the colliding pair of molecules after a collision, $f_{\mathrm{rel}}^{(0)}(q)$ is a Maxwell–Boltzmann distribution function in the reduced relative translational energy, m is the mass of a colliding molecule, and $\bar\sigma^{(\mathrm{tot})}(qij \to q'mn)$ is the degeneracy-averaged, j-averaged, and j'-summed (total) cross section for the transition from pair state $| qij\rangle$ to pair state $| q'mn\rangle$.

The rate equations as expressed here are perhaps in a form unfamiliar to the experimentalist. For this reason it is useful to show that Eqs. (43) do indeed give rise to results which resemble those obtained by other authors who have employed phenomenological arguments. This is best illustrated by examining the simplest such system, that having two vibrational degrees of freedom in addition to translational and rotational degrees of freedom. Equations (43) give for this case

$$[\mathscr{I}_{00} - im\Omega C_v^{(\mathrm{t+r})}/k_{\mathrm{B}}]\,\Delta\hat{T}_m + \sum_{l=1}^{2} \mathscr{I}_{0l}\,\Delta\hat{x}_{ml} = 0$$

$$\mathscr{I}_{k0}\,\Delta\hat{T}_m + \sum_{l=1}^{2} \mathscr{I}_{kl}\,\Delta\hat{x}_{ml} - im\Omega x_k^{(0)}\,\Delta\hat{x}_{mk} = W_{m,k}\,, \qquad k = 1, 2 \tag{67}$$

From the auxiliary condition (42), $\Delta\hat{x}_{m2}$ can be expressed in terms of $\Delta\hat{x}_{m1}$ as

$$\Delta\hat{x}_{m2} = -x_1^{(0)}\,\Delta\hat{x}_{m1}/x_2^{(0)} \tag{68}$$

This, when employed with the relations (46) and (48), lead to a reduction of (67) to the equivalent formulae

$$[(\epsilon_1 - \epsilon_2)^2 \mathscr{J}_{11} - im\Omega C_v^{(\mathrm{t+r})}/k_{\mathrm{B}}]\, \Delta\hat{T}_m - (\epsilon_1 - \epsilon_2)(\mathscr{J}_{11}/x_2^{(0)})\, \Delta\hat{x}_{m1} = 0 \quad (69)$$

and

$$(\epsilon_1 - \epsilon_2)\, \mathscr{J}_{11}\, \Delta\hat{T}_m - (\mathscr{J}_{11}/x_2^{(0)})\, \Delta\hat{x}_{m1} + im\Omega x_1^{(0)}\, \Delta\hat{x}_{m1} = -W_{m,1} \quad (70)$$

the equation for $k = 2$ now being redundant ($W_{m,2} = -W_{m,1}$). The quantity $\Delta\hat{x}_{m1}$ can be eliminated between these two equations to give

$$\begin{aligned}\Delta\hat{T}_m = &-(\epsilon_1 - \epsilon_2)\, \mathscr{J}_{11}(W_{m,1}/x_2^{(0)})[m^2\Omega^2(C_v^{(\mathrm{t+r})}/k_{\mathrm{B}})\, x_1^{(0)} \\ &+ im\Omega(C_v^{(\mathrm{t+r})}\mathscr{J}_{11}/k_{\mathrm{B}}x_2^{(0)}) + (\epsilon_1 - \epsilon_2)^2\, x_1^{(0)}\mathscr{J}_{11})]^{-1} \qquad (71)\end{aligned}$$

A rearrangement of the result (71) into complex exponential form gives

$$\begin{aligned}\Delta\hat{T}_m = &[-(\epsilon_1 - \epsilon_2)\, W_{m,1}k_{\mathrm{B}}/im\Omega C_v] \\ &\times \{1 + (m\Omega C_v^{(\mathrm{t+r})}/C_v)^2(x_1^{(0)}x_2^{(0)}/\mathscr{J}_{11})^2\}^{1/2}\, e^{-i\gamma} \qquad (72)\end{aligned}$$

where C_v is the total heat capacity at constant volume $C_v = C_v^{(\mathrm{t+r})} + C_v^{(\mathrm{v})}$ and γ is defined through

$$\tan\gamma = -mC_v^{(\mathrm{t+r})}x_1^{(0)}x_2^{(0)}/\mathscr{J}_{11}C_v \quad (73)$$

with $C_v^{(\mathrm{v})}/k_{\mathrm{B}}$ for the two-level system given by

$$C_v^{(\mathrm{v})}/k_{\mathrm{B}} = x_1^{(0)}x_2^{(0)}(\epsilon_1 - \epsilon_2)^2 \quad (74)$$

($\epsilon_k \equiv \beta\hbar\omega_k$). As has been mentioned already, the matrix element $\mathscr{J}_{11}$ can be expressed in terms of rate coefficients $k_{ij\to mn}$ according to Eq. (65) as

$$\mathscr{J}_{11} = -nx_1^{(0)}x_2^{(0)}(3k_{12\to 11} + k_{12\to 22}) \equiv -\tau^{-1}x_1^{(0)}x_2^{(0)} \quad (75)$$

The negative sign is due to the fact that the collision operator $\mathscr{J}^{(0)}$ is negative-definite and τ is the relaxation time associated with the decay of the upper level. Notice that the processes represented by the rate coefficients appearing in Eq. (75) are all energetically inelastic, there being no elastic or resonant collision processes contributing to the decay.

In most spectrophones a broadband radiation field is employed and only the fundamental chopper frequency is monitored: hence m in Eqs. (72) and (73) should have magnitude one. When this is allowed for and the results combined with Eq. (37), $\varDelta\hat{T}$ as would be observed in the standard experiment for a two-level system is given by

$$\varDelta\hat{T}(t)=\frac{B_{21}I\sum_n h_{1-n}h_n(x_1^{(0)}-x_2^{(0)})(\epsilon_2-\epsilon_1)\,k_{\mathrm{B}}}{\varOmega C_v}\,\frac{\cos(\varOmega t-\gamma-\frac{1}{2}\pi)}{[1+\varOmega^2\tau^2(C_v^{(\mathrm{t+r})}/C_v)^2]^{1/2}} \tag{76}$$

with the Einstein B-coefficient B_{21} being

$$B_{21}=2\pi\mid\mu_{21}\mid^2/3\hbar^2 \tag{77}$$

The equations describing the optic–acoustic effect, developed from a microscopic kinetic equation, have been demonstrated to reduce in the two-level case to a form similar to that usually written down on the basis of phenomenological considerations. Microscopically derived rate equations bridge the gap between the fundamental kinetic equation governing the behavior of a polyatomic gas and the rate equations which are assumed as the starting point of the conventional phenomenological theories.(8) A general set of coupled rate equations was developed because few polyatomic molecules have a small number of accessible vibrational levels. Despite this, it is sometimes possible in special cases to approximate the vibrational level system by a small number of levels (each of which consists of many strongly coupled levels). It is, for example, a reasonably straightforward exercise to particularize the general set of rate equations presented here [Eqs. (43)] to the case of a three-level system, the model frequently proposed and employed in the analysis(9) of spectrophone results for CO_2.

APPENDIX. COLLISION OPERATOR MATRIX ELEMENTS IN TERMS OF RATE COEFFICIENTS OR COLLISION CROSS SECTIONS

The linearized collision operator employed in this paper has the form

$$\begin{aligned}\mathscr{J}^{(0)}\phi&=(2\pi)^4\,\hbar^2\,\mathrm{tr}_1\int d\mathbf{p}_1\,d\mathbf{q}'\,f_1^{(0)}(p_1)\,\bar{t}_{qq'}[\phi(\mathbf{p}')+\phi_1(\mathbf{p}_1')]\,t_{q'q}^{\dagger}\\&\quad-i(2\pi)^3\,\hbar^2\,\mathrm{tr}_1\int d\mathbf{p}_1\,f_1^{(0)}(p_1)\{t_{qq}[\phi(\mathbf{p})+\phi_1(\mathbf{p}_1)]\\&\quad-[\phi(\mathbf{p})+\phi_1(\mathbf{p}_1)]\,t_{qq}^{\dagger}\}\end{aligned}$$

and the collision operator matrix elements between vibrational levels represented by φ_k and φ_l are given by Eq. (44). Utilizing the explicit form for the φ's as given in Eq. (31) and noting that since φ_k commutes with $f^{(0)}$, the cyclic property of the trace can be employed to convert the latter part of the matrix elements, via the optical theorem,

$$t_{qq} - t^{\dagger}_{qq} = -2\pi i \int d\mathbf{q}'\, \bar{t}_{qq'} t^{\dagger}_{q'q}$$

into a bilinear form. Then, upon converting to center-of-mass and relative coordinates and integrating out the center-of-mass momentum, the result

$$n(\mathscr{J}^{(0)}\varphi_k\,,\ \varphi_l) = (2\pi)^4\, \hbar^2 \operatorname{tr} \operatorname{tr}_1 \int d\mathbf{q}\, d\mathbf{q}'\, f^{(0)} f^{(0)}_{1(\mathrm{int})} \{\bar{t}_{qq'}(\varphi_k + \varphi_{k_1})\, t^{\dagger}_{q'q}\varphi_l - (\varphi_k\, \delta_{kl} + \varphi_{k_1}\varphi_l)\, \bar{t}_{qq'} t^{\dagger}_{q'q}\} \tag{A1}$$

emerges. Note that $f^{(0)}$ is given as the product of $f^{(0)}_{\mathrm{rel}}(q)$ and $f^{(0)}_{\mathrm{int}}$, with $f^{(0)}_{\mathrm{int}}$ given in Eq. (59) as the product of the rotational and vibrational distribution functions, and $f^{(0)}_{\mathrm{rel}}(q)$ given by

$$f^{(0)}_{\mathrm{rel}}(q) = (\pi m k T)^{-3/2} \exp(-q^2/mkT)$$

Now, noting that $f^{(0)}_{\mathrm{vib}}$ can be written in terms of the vibrational populations as

$$f^{(0)}_{\mathrm{vib}} \mid \alpha\rangle = x^{(0)}_{\alpha} \mid \alpha\rangle$$

with the $x^{(0)}_{\alpha}$ having the property

$$\sum_{\alpha} x^{(0)}_{\alpha}\, \delta(\omega_{\alpha}\,,\ \omega_k) = x^{(0)}_k$$

the trace over the vibrational states can be evaluated in Eq. (A1) to give

$$\begin{aligned} n(\mathscr{J}^{(0)}\varphi_k\,,\ \varphi_l) = {} & (2\pi)^4\, \hbar^2 \operatorname{tr}^{\mathrm{rot}} \operatorname{tr}^{\mathrm{rot}}_1 \int d\mathbf{q}\, d\mathbf{q}'\, f^{(0)}_{\mathrm{rel}}(q) f^{(0)}_{\mathrm{rot}} f^{(0)}_{1,\mathrm{rot}} \\ & \times \sum_{\alpha\alpha_1} \sum_{\beta\beta_1} x^{(0)}_{\alpha} x^{(0)}_{\alpha_1} \langle \alpha\alpha_1 \mid \bar{t}_{qq'} \mid \beta\beta_1\rangle\langle\beta\beta_1 \mid t^{\dagger}_{q'q} \mid \alpha\alpha_1\rangle \\ & \times \{\delta(\omega_{\beta}\,,\ \omega_k)\, \delta(\omega_{\alpha}\,,\ \omega_l) + \delta(\omega_{\beta_1}\,,\ \omega_k)\, \delta(\omega_{\alpha}\,,\ \omega_l) \\ & - \delta(\omega_{\alpha}\,,\ \omega_k)\, \delta_{kl} - \delta(\omega_{\alpha_1}\,,\ \omega_k)\, \delta(\omega_{\alpha}\,,\ \omega_l)\} \end{aligned} \tag{A2}$$

If the rate coefficient $k_{\alpha\alpha_1\to\beta\beta_1}$ is defined as

$$\begin{aligned} k_{\alpha\alpha_1\to\beta\beta_1} = {} & (2\pi)^4\, \hbar^2 \operatorname{tr}^{\mathrm{rot}} \operatorname{tr}^{\mathrm{rot}}_1 \int d\mathbf{q}\, d\mathbf{q}'\, f^{(0)}_{\mathrm{rel}}(q)\, f^{(0)}_{\mathrm{rot}} f^{(0)}_{1,\mathrm{rot}} \\ & \times \langle \alpha\alpha_1 \mid \bar{t}_{qq'} \mid \beta\beta_1\rangle\langle\beta\beta_1 \mid t^{\dagger}_{q'q} \mid \alpha\alpha_1\rangle \end{aligned} \tag{A3}$$

Eq. (A2) can be expressed as

$$\begin{aligned} n(\mathscr{J}^{(0)}\varphi_k\,,\ \varphi_l) = \sum_{\alpha\alpha_1}\sum_{\beta\beta_1} x_\alpha^{(0)} x_{\alpha_1}^{(0)} k_{\alpha\alpha_1\to\beta\beta_1}\{&\delta(\omega_\beta\,,\ \omega_k)\,\delta(\omega_\alpha\,,\ \omega_l) \\ &+ \delta(\omega_{\beta_1}\,,\ \omega_k)\,\delta(\omega_\alpha\,,\ \omega_l) - \delta(\omega_\alpha\,,\ \omega_k)\,\delta_{kl} \\ &- \delta(\omega_{\alpha_1}\,,\ \omega_k)\,\delta(\omega_\alpha\,,\ \omega_l)\} \end{aligned} \tag{A4}$$

For the case in which there are no degeneracies, and utilizing the symmetry properties

$$k_{ij\to mn} = k_{ji\to nm}\,, \qquad x_i^{(0)} x_j^{(0)} k_{ij\to mn} = x_m^{(0)} x_n^{(0)} k_{mn\to ij} \tag{A5}$$

of the k's, the expression given in Eq. (A4) can easily be reduced to that given in Eq. (65).

The trace over the rotational states appearing in Eq. (A3) can be expressed as

$$\begin{aligned} k_{\alpha\alpha_1\to\beta\beta_1} = (2\pi)^4\,\hbar^2 \sum_{jj'j_1j_1'} \int d\mathbf{q}\, d\mathbf{q}'\, f_{\text{rel}}^{(0)}(q) f_j^{(\text{rot})} f_{j_1}^{(\text{rot})}\, \delta\Big(\frac{q^2}{m} + \epsilon_{\alpha j} \\ + \epsilon_{\alpha_1 j_1} - \frac{q'^2}{m} - \epsilon_{\beta j'} - \epsilon_{\beta_1 j_1'}\Big)\, |\langle \alpha j m \alpha_1 j_1 m_1 \mid t_{qq'} \mid \beta j' m' \beta_1 j_1' m_1' \rangle|^2 \end{aligned} \tag{A6}$$

This can be expressed, instead, in terms of the collision cross section defined by[7]

$$\begin{aligned} \sigma(q\alpha j m \alpha_1 j_1 m_1 \to q'\beta j' m' \beta_1 j_1' m_1') \equiv \tfrac{1}{4}(2\pi)^4\hbar^2 m^2 (q'/q) \\ \times |\langle \alpha j m \alpha_1 j_1 m_1 \mid t_{qq'} \mid \beta j' m' \beta_1 j_1' m_1' \rangle|^2 \end{aligned} \tag{A7}$$

where q' is understood to be obtained from $E_{q\alpha j m \alpha_1 j_1 m_1} = E_{q'\beta j' m' \beta_1 j_1' m_1'}$. Since $f^{(\text{rot})}$ does not depend on the m quantum number, it is possible to employ directly the degeneracy-averaged cross section defined through

$$\begin{aligned} (2j+1)(2j_1+1)\bar{\sigma}(q\alpha j \alpha_1 j_1 \to q'\beta j' \beta_1 j_1') \\ \equiv \sum_{\substack{mm_1\\ m'm_1'}} \sigma(q\alpha j m \alpha_1 j_1 m_1 \to q'\beta j' m' \beta_1 j_1' m_1') \end{aligned} \tag{A8}$$

Making use of Eqs. (A7) and (A8), and performing the integration over the magnitude of q', Eq. (A5) becomes

$$k_{\alpha\alpha_1\to\beta\beta_1} = \frac{2}{m}\sum_{jj'}\sum_{j_1j_1'} \int d\mathbf{q}\, f_{\text{rel}}^{(0)}(q)\, g_j g_{j_1} q \bar{\sigma}^{(\text{tot})}(q\alpha j \alpha_1 j_1 \to q'\beta j' \beta_1 j_1') \tag{A9}$$

where the cross section entering is now the total cross section

$$\sigma^{(\mathrm{tot})}(q\alpha j\alpha_1 j_1 \rightarrow q'\beta j'\beta_1 j_1') = \int d\Omega_{q'}\, \bar{\sigma}(q\alpha j\alpha_1 j_1 \rightarrow q'\beta j'\beta_1 j_1') \qquad \text{(A10)}$$

Notice that the g_j represent the fractional rotational populations within a given vibrational state and so obey the relation $\sum_j g_j = 1$. If, now, a j-averaged and j'-summed cross section defined as

$$\sigma^{(\mathrm{tot})}(q\alpha\alpha_1 \rightarrow q'\beta\beta_1) = \sum_{jj_1} \sum_{j'j_1'} g_j g_{j_1} \sigma^{(\mathrm{tot})}(q\alpha j\alpha_1 j_1 \rightarrow q'\beta j'\beta_1 j_1') \qquad \text{(A11)}$$

is introduced, the expression given in Eq. (66) is obtained.

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